PATENT SPECIFICATION

(11) 1 505 077

(21) Application No. 28804/74 (22) Filed 28 June 1974
(23) Complete Specification filed 20 June 1975
(44) Complete Specification published 22 March 1978
(51) INT CL^2 C09J 5/00
(52) Index at acceptance
B5K 3
C3C 128 164 184 366 520
(72) Inventor CHRISTOPHER VALLANCE

(19)

1 505 077

(54) POROUS DIAPHRAGMS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in the manufacture of porous diaphragms.

More particularly, the invention relates to improvements in the manufacture of porous diaphragms suitable for use in electrolytic cells.

Porous diaphragms based on tetrafluoroethylene polymers are especially suitable for use in cells for the electrolysis of alkali metal chloride solutions. In our UK Patent Specification No. 1,081,046 there is described a method of manufacturing such diaphragms which comprises forming a filled polytetrafluoroethylene sheet from an aqueous dispersion of polytetrafluoroethylene and a removable solid particulate additive, e.g. starch, by adding an organic coagulating agent such as acetone to said dispersion and then drying the coagulated dispersion. An organic lubricant such as petroleum ether is then added to the dried coagulated material to serve as a processing aid when the material is being rolled into a sheet. On completion of the rolling operation the starch is removed from the sheet to give the desired porous diaphragm. The lubricant can also be removed if required.

Another method of manufacturing such porous diaphragms in which the organic lubricant is replaced by water as lubricant is described of our UK Patent Specification No. 1,424,804. This method comprises forming a filled polytetrafluoroethylene sheet from an aqueous dispersion comprising polytetrafluoroethylene and a removable solid particulate additive by thickening said aqueous dispersion to effect agglomeration of the solid particles therein, forming from the thickened dispersion a sheet-formable material containing sufficient water to serve as lubricant in a subsequent sheet forming operation, forming a sheet of desired thickness from said material, for example by passing material through calendar rolls, and removing solid particulate additive from the sheet. As indicated above, suitable removable solid particulate additives include starch, e.g. maize and/or potato starch. Other removable additives are water-insoluble inorganic bases or carbonates, e.g. calcium carbonate. Cellulose also is a suitable additive. If desired, these solid particulate additives, which constitute the means of imparting porosity to the diaphragm, may be removed from the diaphragm prior to introducing the diaphragm into the electrolytic cell. Alternatively, the solid particulate additives may be removed from the diaphragms *in situ* in the cell.

Hereafter in this specification and claims the term filled polytetrafluoroethylene sheet shall mean polytetrafluoroethylene sheet containing removable solid particulate additive.

Unfortunately, however, there are problems associated with the development of the use of such diaphragms in electrolytic cells. For example, there is generally a limit on the dimensions of the diaphragm sheets that can be produced in practice. Of necessity the width of the diaphragm sheet is governed by the size of the rolls employed in producing the sheet. The cost of increasing the size of the manufacturing equipment is exponential with the result that there is an optimum size of roll which is dependent upon purely commercial factors. Moreover, diaphragms of simple rectangular sheet form are extremely difficult to fit onto the complicated cathode designs of modern diaphragm cells because of the numerous recesses and protuberances presented by the cathode. The aforesaid problems are accentuated in the case of diaphragms made of non-melt-processable materials such as PTFE. The main reason for this is

that it is extremely difficult to join together small sheets of polytetrafluoroethylene in order to produce a diaphragm of the desired complex shape and size. It is an object of the present invention to provide a method of manufacturing polytetrafluoroethylene diaphragms which obviates or mitigates the aforesaid disadvantages.

According to the present invention there is provided a method of manufacturing a porous diaphragm for an electrolytic cell from a plurality of sheets of filled polytetrafluoroethylene (as hereinbefore defined) which method comprises fusing a melt-processable fluorine-containing polymer (as hereinafter defined) into said sheets at or near juxtaposed edges of said sheets at a temperature which will not substantially decompose the filler in said sheets, solidifying the melt-processable polymer so as to effect joining of the sheets, and thereafter removing filler from the thus joined sheets.

By melt-processable fluorine-containing polymer we mean a fluorine-containing polymer which may be fused by the application of heat and which returns to its original form on removal of heat and also retains its original properties.

In one embodiment of the invention two or more sheets of filled polytetrafluoroethylene are joined along juxtaposed edges by overlapping said edges with one or more strips of melt-processable fluorine-containing polymer and fusing said strip or strips into the areas of the sheets adjacent to said juxtaposed edges.

However, in a preferred embodiment of the invention one or more strips of melt-processable fluorine-containing polymer can be made to partially overlap one or more edges of a sheet of filled polytetrafluoroethylene and protruding portions of said strip or strips can be utilised as desired to bond said polytetrafluoroethylene sheet to other polytetrafluoroethylene sheets which have not had melt-processable strips of fluorine-containing polymer fused thereto. Conveniently all four sides of a rectangular sheet of filled polytetrafluoroethylene can be provided with overlapping strips of melt-processable fluorine-containing polymer to give a window-frame effect and such unit window-frames of melt-processable polymer can be joined to other filled polytetrafluoroethylene sheets by conventional plastics fabrication techniques.

The last mentioned procedure can be modified by replacing the strips of melt-processable fluorine-containing polymer with tabs of melt-processable polymer at intervals along one or more edges of a filled polytetrafluoroethylene sheet.

As aforesaid, the melt-processable fluorine-containing polymer must be such that it fuses into the filled polytetrafluoroethylene sheet below the temperature at which the filler substantially decomposes. For example, in the case where the filler is starch, the upper temperature for the fusion process must not exceed 300°C. Furthermore, it is important that the melt-processable polymer be impermeable or of the same porosity as the eventual polytetrafluoroethylene diaphragm. Consequently the temperature at which fusion takes place must be so high as to allow decomposition products to blow holes in the melt-processable polymer.

When the diaphragm manufactured according to the present invention is intended for use in electrolytic cells then the melt-processable fluorine-containing polymer must be resistant to conditions in the cell.

The melt-processable fluorine-containing polymer used in the present invention is one which substantially returns to its original form on the removal of heat and also retains its original properties. By comparison, polytetrafluoroethylene, which is considered as a non-melt-processable material in the context of the present invention, fuses when heat is applied but also decomposes within a few degrees of its melting point. In other words the melt viscosity of polytetrafluoroethylene is too high for the application of conventional plastics fabrication techniques.

Preferably, the melt-processable fluorine-containing polymer is selected from polychlorotrifluoroethylene, polyvinylidene fluoride, FEP (a fluorinated ethylene/propylene copolymer) or a copolymer of ethylene and chlorotrifluoroethylene.

Conveniently the melt-processable fluorine-containing polymer is fused into the filled polytetrafluoroethylene sheet by the application of heat and pressure. The temperature at which the melt-processable polymer is fused into the polytetrafluoroethylene sheet preferably is lower than the melting point of polytetrafluoroethylene. The temperatures and pressures employed depend upon the specific melt-processable polymer involved. We have found, however, that in most cases it is advantageous to operate at a constant pressure of around 10 psi and to apply heat over a varying period of time which does not result in deformation of the diaphragm.

The present invention is also a porous polytetrafluoroethylene diaphragm

whenever manufactured by a process as hereinbefore described.

The diaphragms of the invention may contain a non-removable filler such as titanium dioxide in order to render the diaphragm wettable when installed in an electrolytic cell.

Embodiments of the invention will now be described with reference to the following Examples in which all parts and percentages are by weight.

Example 1

To 100 parts of an aqueous dispersion of polytetrafluoroethylene containing 60% of polymer substantially all of which was in the form of particles in the size range 0.15 to 0.2 micron were added 101 parts of water, 60 parts of titanium dioxide of particle size approximately 0.2 micron, 60 parts of maize starch of particle size approximately 13 microns and 120 parts of potato starch of particle size less than 75 microns. The aqueous mixture was then stirred with a paddle-mixer for 30 minutes to form a substantially uniform paste. This paste was spread on trays and dried at 24° for 48 hours to a water content of 5.7%. 100 parts of the resultant crumb were mixed with 52 parts of water to form a sheet-formable material akin to a dough having a viscosity of 4×10^6 poise. The sheet-formable material was then spread along the shortest edge of a rectangular piece of card, and calendered on the card between dual, even-speed, calender rolls, set 3 mm apart, into an oblong sheet. After calendering, the oblong sheet was cut, in the direction of calendering, into four equal pieces. These were laid congruently over each other to obtain a four-layered laminate. The card was picked up, rotated 90° in the horizontal plane, and calendered (directed 90° to the original direction of calendering) again through the 3 mm roll separation. This process, the successive cutting into four, stacking, rotating and calendering was repeated until the composition had been rolled a total of five times. The resultant laminate was cut into four, in the direction of calendering, stacked, removed from the card, and calendered, without rotation through 90°, the inter-roll space being reduced by the thickness of the card. After calendering, the laminate was cut, at right angles to the direction of calendering, into four equal pieces, stacked, rotated through 90° and calendered again. This process, cutting at right angles to the direction of calendering, stacking, rotating and calendering was repeated until the composition had been rolled a total of nine times. The resultant essentially rectangular laminate was then passed through the rolls with its largest side directed at 90° to the direction of calendering, and with the inter-roll space slightly reduced, no cutting, stacking or rotating through 9° being involved. This process was repeated through a gradually reduced inter-roll space, the same edge of the laminate being fed to the rolls on each occasion, until the thickness of the laminate was 1.5 mm. A square of 22x26 mesh gauze woven of 0.011 inch diameter monofilament polypropylene yarn was placed on top of the laminate, and rolled into the laminate by calendering through a slightly reduced inter-roll space.

The edges of two sheets of filled polytetrafluoroethylene prepared as above were brought together in a butt-joint and a strip of FEP of thickness 0.02 inches was laid along the length of the butt-joint. This composite join was then heated by means of heated platens under a pressure of 10 psi for a period of 10 minutes until a temperature of 275°C was attained. By this means an adequate joining of the two PTFE sheets was effected, charring of the starch being minimised.

The aforesaid sample of joined PTFE sheets was then immersed in 5N HCl in order to remove the starch filler. A porous PTFE diaphragm suitable for use in diaphragm a cell was produced. After removal of the starch, the PTFE/FEP joint was still effective.

Example 2

Two starch filled PTFE sheets prepared according to Example 1 but with an FEP backing sheet instead of polypropylene were joined together at their edges by means of a strip of FEP of thickness 0.01 inches. The welding took place between parallel flat heating elements $^5/_{16}$ inch wide and under a pressure of 4 psi. The elements were lightly greased with silicone grease to prevent sticking. Pressure was maintained on the weld for 30 seconds after turning off the welding current. The maximum temperature attained was 280°C and was measured between the interfaces of the materials with a dwell time of between one and two seconds.

The sample of joined PTF sheets was immersed in 5N HCl in order to remove the starch filler. A porous PTFE diaphragm suitable for use in a diaphragm cell was produced.

Example 3

Two PTFE sheets prepared according to Example 1 but with cellulose as filler and with FEP backing sheet were joined together by the technique of Example 2 with the exception that current was only supplied to the element in contact with the 0.01 inches thick FEP strip to prevent

undue degradation of the cellulose. An adequate join was obtained and the cellulose filler was removed by immersing the sheets in 5N HCl to give a porous PTFE diaphragm.

Example 4

The juxtaposed edges of two PTFE sheets prepared according to Example 1 with starch as filler and each having an FEP backing sheet had juxtaposed edges joined together by the technique of Example 2 except that a strip of Halar (a copolymer of ethylene and chlorotrifluoro ethylene) (Halar is a Registered Trade Mark) of thickness 0.005 inches was placed over the butt joint, in place of the FEP and with a maximum temperature 260°C was used. An adequate joining of the two PTFE sheets was effected and the starch was removed as before to give a porous diaphragm.

WHAT WE CLAIM IS:—

1. A method of manufacturing a porous diaphragm for an electrolytic cell from a plurality of sheets of filled polytetrafluoroethylene (as hereinbefore defined) which method comprises fusing a melt-processable fluorine-containing polymer (as hereinbefore defined) into said sheets at or near juxtaposed edges of said sheets at a temperature which will not substantially decompose the filler in said sheets, solidifying the melt-processable polymer so as to effect joining of the sheets, and thereafter removing filler from the thus joined sheets.

2. A method as claimed in claim 1 wherein the melt-processable fluorine-containing polymer is resistant to conditions in an electrolytic cell.

3. A method as claimed in claim 1 or claim 2 wherein the melt-processable fluorine-containing polymer is polychlorotrifluoroethylene, polyvinylidene fluoride, a fluorinated ethylene/propylene copolymer or an ethylene/chlorotrifluoroethylene copolymer.

4. A method as claimed in any one of the preceding claims wherein the melt-processable fluorine-containing polymer is fused into the polytetrafluoroethylene sheet by the application of heat and pressure.

5. A method as claimed in any one of the preceding claims wherein the temperature at which the melt-processable fluorine-containing polymer is fused into the polytetrafluoroethylene sheet is lower than the melting point of polytetrafluoroethylene.

6. A method of manufacturing a porous diaphragm for an electrolytic cell substantially as hereinbefore described.

7. A porous diaphragm whenever prepared by the method of any one of claims 1 to 6.

8. An electrolytic cell fitted with the diaphragm of claim 7.

A. McPHERSON,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/000388

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B29C65/00 B29C65/50 C08J5/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B29C C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 505 077 A (ICI LTD) 22 March 1978 (1978-03-22) page 2, line 39 - line 60 page 2, line 89 - line 126 page 3, line 79 - line 90; example 4	1-30
A	EP 0 002 894 A (ICI PLC) 11 July 1979 (1979-07-11) page 10, line 10 - line 30 page 12, line 25 - line 30 page 5, line 9 - line 16	1-30

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 May 2004	04/06/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Attalla, G

1